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EFFECTIVE METHODS OF PROCESSING ARGILLACEOUS MATERIALS FOR BUILDING CERAMICS

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The use of new nontraditional methods for improving the quality of argillaceous materials (mechanical activation, modifications, ultrasonic treatment, electrochemical activation, introducing nontraditional additives, pulsation concentration, etc.) and selecting technological parameters (batch composition, granulometric composition of molding powder, firing schedule, etc.) make it possible to produce building ceramics (bricks, facing tiles, roof tiles) with improved service parameters on the basis of low-grade argillaceous materials from the Republic of Tatarstan.

Products offered by the construction materials industry in the Republic of Tatarstan have little variety and are not of very high quality; therefore, the demand to a large extent is satisfied by importing products from other regions. The problems of this sector of industry are mainly due to the low quality of available mineral materials, insufficient equipment at the enterprises, and use of old technologies that do not allow for high-quality products. Orienting companies toward advanced up-to-date technologies that make it possible to improve quality and expand product ranges is more cost-effective than upgrading and reequipping the companies. The latter involves big capital investments and much time, which makes it not too attractive for investors in view of long repayment periods.

New requirements are currently being imposed on qualitative product parameters. Thus, thermal resistance of fencing should grow 3.5 times, and accordingly, production of wall materials with good heat-insulating parameters becomes a topical problem.

The process of producing ceramics for construction (brick, tile, roof tile) includes the following operations: mixture preparation, molding (plastic or semi-dry), drying, and firing. The novelty of the technologies proposed consists in using nontraditional methods for processing argillaceous materials and in selecting process parameters (batch composition, granulometric composition of molding powder, firing schedule, etc.). The research was carried out in the framework of the State program for studying and reproducing mineral material resources of the Republic of Tatarstan.

Different methods were used in processing materials: mechanical activation and modification (combined treatment

with additives) in a vibration grinder, in a ball mill, and in an electric mixture classifier, ultrasonic treatment, electrochemical activation (using activated water and electrokinetic dehydration), electromagnetic treatment of molded product, introduction of traditional and nontraditional mineral additives, pulsation concentration, and combined schemes.

Mechanic activation affects such properties as refractoriness, mechanical strength, and drying sensitivity. Involving a set of precision physicochemical methods made it possible to identify the reason for structural modifications occurring in argillaceous minerals under mechanical effects. Using gamma-resonance spectroscopy, a relationship was established between the degree of distortion of the crystalline structure of clay minerals and mechanical strength of fired samples. Thus, the mechanical strength of samples based on Sarai-Chekurchinskoe and Klyuchishchenskoe clay deposits in Tatarstan first subjected to mechanical activation in a vibration crusher is higher the greater the quadrupole splitting of Fe^{2+} ions in the structure of montmorillonite. Part of Fe^{3+} ions pass from a less distorted position (having isovalent cations in their immediate environment) to a more distorted position (where Fe^{3+} neighbor heterovalent cations and vacant octahedral positions). X-ray diffraction analysis of mechanically activated samples indicated that the structure of the interlayer space becomes sharply disturbed (the bonds between the interlayer cations and hydroxyl group hydrogen ions weaken), and under a longer activation effect the main structural fragments (octahedral and tetrahedral lattices) as well experience intense deformation as a consequence of deprotonizing processes.

Thus, with an increasing activation duration, interlayer bonds are disturbed in the entire bulk of material. This, in turn, sharply increases the specific surface area of material

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due to the formation of surfactant crystallites with partly non-compensated bonds. The activity of the latter ensures high strength of the finished product.

Mechanical activation of argillaceous materials was performed in a 260.21/22 ball mill (East Germany) and a 75T-DRM vibration crusher. The ratio between the masses of balls and material processed in the mill amounted to 6 : 1. The treatment duration varied from 5 to 30 min (RF Patent No. 2197446).

Natural initial materials can be activated and improved using a SMG-ÉMK-005-1 electric mixture classifier, whose principle is based on new technologies taking into account electrophysical and inertial parameters of particles. Friable powder components are treated in dry form (moisture not more than 7%) in an activation chamber in an enclosed volume. After treatment part of the product is transferred to the fine-fraction receiving hopper, and the other part to the coarse-fraction hopper. The set operates in a batch mode; its output is 50 kg/h.

The electric mixture classifier provides for obtaining fine- and ultra-disperse (ranging from 0.1 to 500 μm) homogeneous powder materials. The treatment of clay materials in the electric mixture classifier raises the strength parameters of ceramics by 25 – 50%.

The use of the pulsation concentration method makes it possible to perform relatively fast attrition of clay particles from granular materials and obtain several clay fractions for subsequent selection of slip consistency. The advantages of this method also include low power consumption and the possibility of introducing different reactants into suspensions (alkalis, electrochemically activated water, etc.). The use of a ceramic mixture concentrator enables one to thicken suspensions, quickly separate the major bulk of water, and recirculate it. Suspension vibration with an amplitude within 16 – 18 cm is provided by air pulses with a period of 7 sec and an impact duration of 2 sec. This treatment method combined with others raises the sinterability of argillaceous materials and improves the main physicomechanical properties of ceramics. At the same time, the materials acquire better colorability parameters and have more homogeneous and saturated tints.

The quantity of natural materials can be improved as well by an electrokinetic effect on the slip. This causes electro-osmotic dehydration accompanied by drying of the initial clay materials, electrophoretic transfer of charged particles in the electric field and, consequently, activation of clay minerals. All these processes are in direct dependence on the composition and structural modifications of minerals and also on the nature and quantitative parameters of the electric field applied. Electrokinetic technology allows for using argillaceous materials contaminated with carbonate, stony, and other inclusions, with a simultaneous 2 – 4-fold decrease in energy consumed in moisture removal, whereas electrochemical activation of argillaceous minerals in dehy-

dration also increases the strength of ceramics based on mixtures treated in this way.

A plant for dehydration and activation of ceramic slips consists of a direct current source U-300 of power 1 kW, a G5-54 pulse generator with frequencies up to 10⁵ Hz, a non-standard pulse power amplifier, electric measuring instruments, an aluminum plate with holes of diameter 1 mm acting as the anode, and a cell of size 200 × 100 × 100 mm assembled from textolite and tin mesh with holes 0.25 × 0.25 mm acting as the cathode. The cell design prevents inhomogeneity in filtration moisture transfer and to a maximum extent approaches probable production conditions on a continuous plant (RF Patent No. 1790499).

Ultrasonic treatment of ceramic mixtures is promising as well. Optimum regimes for treating clay suspensions have been selected (ratio solid : liquid = 1 : 20, impact duration 4 and 7 min with frequency of 22 and 44 kHz). The studies were carried out using a UZDN-2T disperser.

Unfired molded products were treated using a magnetic field (constant and variable) within a wide intensity interval, from a few tens to 13,000 Oe. Intense magnetic fields from 2000 to 13,000 Oe were obtained in an electromagnet fed by direct current. Lower values of magnetic field intensity have been registered in coils of a rectangular or round section (solenoid).

Electrochemical activation of argillaceous material consisted of using activated water for diluting a ceramic mixture, which was obtained in the following way. First, 0.1 M solution of sodium nitrate was prepared. An electrochemical activator was placed in the electrolyte and a current passed through it, its strength varying from 3 to 14 A. As a consequence, the pH of water known as “live water” was equal to 8.9 and 9.6.

The most common method for improving the quality of argillaceous material is introducing technological additives for various purposes into a batch. In producing hollow porous bricks, two contradictory problems have to be solved simultaneously: improving sinterability, which results in higher strength, and increasing porosity, which decreases the volume mass and strength of articles. To make a high-quality product, the optimum ratio between fluxes and pore-forming additives should be determined, or “dual-effect” technological additives should be used, which contribute to reaching the required porosity level while preserving or even improving the strength parameters.

The pore-forming additives were peat, bituminous dolomites, carbonate rocks, and wood sawdust, whereas fluxing additives were high-melting and zeolite-containing clays, as well as zeolite-bearing siliceous rocks, the latter being a “dual effect” additive (RF Patents Nos. 2111189, 2140888, 2176223, and 2176224). All materials listed above (except for high-melting clays) can be found on the territory of the Republic of Tatarstan.

The combined method includes elements of the methods specified. Depending on the quality of initial argillaceous

material and the final purpose, a particular treatment method can be used to achieve an optimum result.

The use of the methods considered makes it possible to improve the molding and drying properties and sinterability of clay materials and thus to improve the service parameters of products.

The Central Research Institute of Geology of Nonmetallic Minerals tested technological methods on the line for large-scale technological testing and produced standard product lots (bricks, tiles) meeting the regulatory requirements.

Polymineral argillaceous material from the Republic of Tatarstan was used to produce highly hollow (hollow volume 21, porosity 41%) porous brick with a volume weight of 940 – 980 kg/m³ using the plastic molding method. This brick has strength grades 75 and 100, cold resistance F25 and more, and water absorption 18.1 – 18.6%.

Light-colored bricks (hollowness 11%) made by semidry molding from calciferous clays have volume mass of 1460 – 1565 kg/m³, strength grades 100 – 200, cold resistance F25, and water absorption 18.3 – 24.9%.

A process schedule was developed based on new technologies recommended for production of hollow-porous bricks by plastic molding based on argillaceous materials from Tatarstan. It takes into account technological schemes used at brick factories of Ceric, Agemas, Verdes, Pab Bautzen, and Fuchs companies.

The cost of introducing new technologies is compensated by material saving (up to 40%) and fuel saving (up to 20%) in the production of highly hollow porous bricks (due to hollowness and porosity of ceramics). The production cost of

porous-hollow bricks is 10 – 15% lower than that of standard bricks.

Buildings constructed from porous-hollow bricks with better thermal-engineering parameters require significantly less thermal energy for heating. Heating of buildings in central Russia requires 500 kW · h per m². The use of efficient thermal-insulating materials allows for a 2 – 3-fold decrease in heating cost.

The bending strength of ceramic facing tiles for interior decoration produced by semidry molding is 15.6 – 22.1 MPa, and water absorption 6.5 – 11.9%. Tiles made of light-burning calciferous argillaceous material have satisfactory characteristics as well. Their bending strength is 15 – 17 MPa, and water absorption 19 – 24%. A process schedule for industrial conditions has been developed.

The technology of producing decorative facing ceramic tiles and facing ceramic bricks based on low-melting clays with additives of vermiculite, muscovite, biotite, and phlogopite includes molding, semidry compression, and firing at 900 – 1100°C. The physical properties of the materials meet the prescribed requirements. Mica for imparting decorative properties can be introduced directly into ceramic mixtures or deposited on the product surface.

Argillaceous material from Tatarstan can be used to produce ceramic roof tiles. The estimated destructive load on waterproof roof tile depending on firing temperature is 82 – 129 kgf.

The products developed can be useful for different regions of the Russian Federation, which do not have high-quality argillaceous materials on their territories.